# Michigan Department of Environmental Quality Air Toxics Workgroup

Clean Fuels Discussion April 10, 2013 Draft2

## ORR (2011) Report Recommendation A-1(4):

R 336.1225 should be amended and specifically include the following: Exempt clean fuels such as natural gas, low sulfur #2 fuel oil, and non-chemically treated biofuels.

#### **SUMMARY**

Emissions estimates for processes such as boilers, engines and turbines that burn fuels such as natural gas, low sulfur diesel, and wood are presented. Fenceline air concentrations of toxic air contaminants (TACs) from small, medium and large processes that burn these fuels were compared to Air Quality Division's TAC screening levels (i.e., Initial Threshold Screening Levels, ITSLs and Initial Risk Screening Levels, IRSLs) in order to assess potential health impacts. The fenceline air concentrations of TACs for each fuel, process type and size which resulted in impacts above their respective screening levels are provided in order to evaluate the impacts of a particular process/fuel combination in order to further consider the development of a rule to exempt them from Rule 225.

#### **BACKGROUND**

Relevant current AQD permitting exemptions and requirements:

- a. Rule 285(g) exempts from the requirement to obtain a Permit to Install, engines that have <10 MMBTU/hour maximum heat input.
- b. Rule 282(b) exempts from the requirement to obtain a Permit to Install, several types of fuel and fuel-burning equipment, including natural gas combustion with a rated heat input capacity of not more than 50 MMBTU/hour.
- c. Emission units that do not meet any of the exemptions from the requirement to obtain a Permit to Install must currently undergo R225 review, with one notable exception. In 2006, the AQD suspended enforcement of R225 for certain natural gas combustion engines. This one-year variance has been renewed annually since then. This variance applies to emission units that combust natural gas as fuel and that meet either of the following criteria:
  - Fuel-burning equipment or natural gas fired equipment, with a maximum natural gas usage rate of 50,000 cubic feet per hour or less, where the emissions from the natural gas combustion are discharged unobstructed vertically upwards from an emissions discharge point at least 1.5 times the height of the building most influential in determining the predicted ambient impacts of the emissions.
  - 2. Air pollution control equipment, as defined by Act 451, not limited in the natural gas usage rate.

The justification for the variance for natural gas combustion engines (refer to c. above) is that some of these processes would not meet the requirements of R225 for one or more TACs (acrolein being one), and, requiring compliance with R225 would create an undue hardship and would be out of proportion to the benefits to be obtained by compliance. Natural gas is recognized as an environmentally beneficial, clean burning fuel; there is no better readily available alternative fuel for some sources at this time. Good engineering practice will be

applied to sources that qualify for the variance to assure a continuing level of public health protection.

#### **Key Term**

MMBTU/hour = million British Thermal Units per hour. Emission factors are commonly presented in, or can be converted to, units of pounds of a particular TAC emitted per MMBTU (lbs/MMBTU).

## **General Approach**

The AQD believes that the ORR report's recommendation should be pursued with further information and assessment. A wide range of air toxics are emitted by combustion of these fuels, including VOCs, acid gases, PAHs, acrolein, dioxins/furans and aldehydes. These air toxics pose hazards including carcinogenicity and irritancy. If it can be adequately demonstrated that the ambient air impacts of air toxics from these sources are sufficiently low and that the public health will be protected, then an exemption from R225 would be appropriate. This report summarizes an attempt to quantify emissions and ambient impacts from various clean fuels.

Staff performed modeling exercises to characterize the potential air toxics impacts and public health concerns, if any, for reasonably anticipated sources and scenarios. Air toxics emission factors are being pulled from the EPA's WebFIRE database (EPA, 2013), and air dispersion modeling is being performed using EPA's AIRSCREEN model. The available air toxics screening levels (ITSLs and IRSLs) are used to "screen" modeled impacts. For those fuels, source types and sizes, the air toxics that do not pass this screen, as well as the magnitude of exceedance of the benchmarks are noted. Further evaluation of these exceedances may be warranted in order to assess any potential health risk associated with the proposed exemption from the air toxics rules for a particular fuel/process scenario.

One of the key concepts used to determine emissions for combustion processes is the amount of fuel burned per hour. Emission factors are commonly presented in, or can be converted to, units of pounds of a particular TAC emitted per million British Thermal Units (MMBTU), or lbs/MMBTU. In order to facilitate comparison between the processes, all emission rates were converted to lbs/MMBTU. The size of a particular fuel burning process in generally quantified in heat output per hour, or MMBTU/hour.

#### **METHODOLOGY**

The approach is outlined as follows:

- Appropriate air toxics emission factors are selected, for boilers, turbines, engines, and process heaters. For a particular TAC, the highest emission factor for any of these four source types is selected for the subsequent modeling and evaluation.
- 2. Only indirect combustion sources (processes where the products of combustion do not come in direct contact with a raw material being processed) are included.
- 3. The fuel types evaluated so far are natural gas, diesel fuel (a.k.a., No. 2 fuel oil<sup>1</sup>) and wood/bark. Biodiesel is being considered, but since EPA has no published emission factors (EFs) for biodiesel, a literature search was performed. Once biodiesel EFs are obtained, an impact analysis and comparison to screening levels may be presented for discussion. Other fuel types may be added later.

<sup>&</sup>lt;sup>1</sup> The predominant form of No. 2 fuel oil in use by Michigan facilities today is ultra-low sulfur diesel fuel. However, this is not an important distinction because the available emission factors do not differentiate air toxics emission factors based on the sulfur grade of the fuel.

- 4. For the purposes of this exercise, modeling was performed for relatively small, medium, and large source sizes (50 MMBTU/hour, 100 MMBTU/hour, and 500 MMBTU/hour, respectively). The source size criteria of any eventual R225 exemption are, of course, unknown at this time, and may even be all-inclusive.
- 5. The stack heights for the modeled small, medium, and large sources will be 40', 60', and 80', respectively. These are believed to be fairly representative, for the purposes of this exercise. Other facility parameters (e.g., exit velocity (10 m/s); temperature (250F)) are believed to be reasonable values.
- 6. The assumed ratio of the stack height and building height (Hs/Hb) is 1.5.
- 7. The modeling grid uses 25 m spacing, with 50 m from the stack to the nearest receptor.
- 8. The building dimensions are 100' X 100', and the stack is placed at the center of the building. Therefore, the nearest modeling receptor is approximately 150' from the stack and 100' from the edge of the building.

It should be noted that this methodology incorporates some conservative elements and assumptions. Any modeled air toxics impacts that exceed their screening levels should not necessarily be interpreted to mean that unacceptable public health risks exist and that an exemption is inappropriate. Conservative assumptions include:

- 1. The highest available and appropriate emission factor was selected for each TAC, across the four source and three fuel types.
- 2. The nearest receptor point is fairly close to the building, and the maximum modeled impact was selected.
- 3. The AIRSCREEN model is a screening model, designed to over-predict impacts, as compared to a refined model.
- 4. The public exposure potential was assumed to be continuous, at the point of maximum modeled impact. This may be fairly realistic for screening levels with short averaging times (e.g., 1-8 hr), but this is generally conservative for annual averaging times. For cancer risk assessment and other critical effects associated with chronic exposure, assumed continuous lifetime exposure at the point of maximum modeled impact is conservative.
- 5. Air toxics screening levels generally have substantial uncertainty, and are designed to be protective of the public including sensitive subgroups. Generally speaking, a modest amount of ITSL exceedance would not be expected to necessarily result in adverse health effects. Cancer risk estimates are based on generally conservative extrapolation to low-risk estimates, using "plausible upper-bound" modeling.

# **Preliminary Results**

## A. Natural gas

A total of 76 TACs had available appropriate emission factors for natural gas, for at least one of the four source types. Most EFs were for engines or boilers; process heaters had EFs only for formaldehyde. The TACs that had maximum modeled impacts exceeding an ITSL or IRSL were as follows:

Source Size		SL*	SL		Magnitude of SL	
(MMBTU/hr)	Chemical Name	Type	(µg/m³)	AT**	exceedance***	Process Type
50	1,3-Butadiene	IRSL	0.03	annual	3.0	Recip. engine
50	Acetaldehyde	IRSL	0.5	annual	1.8	Recip. engine
50	Acrolein	ITSL	5	1 hr	1.7	Recip. engine
50	Acrolein	ITSL	0.02	annual	42.2	Recip. engine
50	Ethylene dibromide	IRSL	0.002	annual	4.0	Recip. engine
100	1,3-butadiene	IRSL	0.03	Annual	3.9	Recip. engine
100	Acetaldehyde	IRSL	0.5	Annual	2.4	Recip. engine
100	Acrolein	ITSL	5	1 hr	2.2	Recip. engine
100	Acrolein	ITSL	0.02	Annual	56	Recip. engine
100	Ethylene dibromide	IRSL	0.002	Annual	5.3	Recip. engine
500	1,1,2,2-					
	Tetrachloroethane	IRSL	0.02	annual	1.7	Recip Engine
500	1,3-Butadiene	IRSL	0.03	annual	13.9	Recip Engine
500	1,3-Butadiene	ITSL	2	24 hr	1.25	Recip Engine
500	Acetaldehyde	ITSL	9	24 hr	2.8	Recip Engine
500	Acetaldehyde	IRSL	0.5	annual	8.5	Recip Engine
500	Acrolein	ITSL	5	1 hr	7.9	Recip Engine
500	Acrolein	ITSL	0.02	annual	198.0	Recip Engine
500	Ethylene dibromide	IRSL	0.002	annual	18.6	Recip Engine

<sup>\*</sup>Screening Level: Initial Threshold Screening Level (ITSL); Initial Risk Screening Level (IRSL)

<sup>\*\*</sup> AT = Averaging Time associated with Screening Level

<sup>\*\*\*</sup>cancer risk in 1 million, or noncancer Hazard Quotient

## B. Diesel fuel

A total of 36 TACs had available appropriate emission factors for diesel fuel, for at least one of the four source types. The TACs that had maximum modeled impacts exceeding an ITSL or IRSL were as follows:

Source Size (MMBTU/hr)	Chemical Name	SL* Type	SL (µg/m³)	AT**	Magnitude of SL exceedance***	Process Type
50	Arsenic	IRSL	0.0002	Annual	6.0	Engine turbine
50	Benzene	IRSL	0.1	Annual	1.01	Engine recip.
50	Chromium VI	IRSL	8.3E-5	Annual	1.44	Engine turbine
50	Manganese	ITSL	0.05	Annual	1.71	Engine turbine
100	Arsenic	IRSL	0.0002	Annual	7.9	Engine turbine
100	Benzene	IRSL	0.1	Annual	1.3	Engine recip.
100	Beryllium	IRSL	0.0004	Annual	1.1	Boiler
100	Cadmium	IRSL	0.0006	Annual	1.2	Engine turbine
100	Chromium VI	IRSL	8.3E-4	Annual	1.9	Engine turbine
100	Manganese	ITSL	0.05	Annual	2.3	Engine turbine
500	Acetaldehyde	IRSL	0.5	Annual	1.1	Engine Recip
500	Acrolein	ITSL	0.02	Annual	2.4	Engine Recip
500	Arsenic	IRSL	0.0002	Annual	28.0	Engine turbine
500	Benzene	IRSL	0.1	Annual	4.7	Engine Recip
500	Beryllium	IRSL	0.0004	Annual	3.8	Boiler
500	Cadmium	IRSL	0.0006	Annual	4.1	Engine turbine
500	Chromium VI	IRSL	8.3E-5	Annual	6.7	Engine turbine
500	Formaldehyde	IRSL	0.08	Annual	3.0	Engine Recip
500	Manganese	ITSL	0.05	Annual	8.0	Engine turbine

<sup>\*</sup>Screening Level: Initial Threshold Screening Level (ITSL); Initial Risk Screening Level (IRSL)

<sup>\*\*</sup> AT = Averaging Time associated with Screening Level

<sup>\*\*\*</sup>cancer risk in 1 million, or noncancer Hazard Quotient

#### C. Wood Fired Boilers

A total of 129 TAC Emission Factors were available for wood fired boilers. The TACs that had

maximum modeled impacts exceeding an ITSL or IRSL were as follows:

Source	modeled impacts exec	SL*	SL		Magnitude of SL	Process
Size (MMBTU/hr)	Chemical Name	Type	(µg/m³)	AT**	exceedance***	Type
50	Acrolein	ITSL	0.02	annual	21.72	Wood boiler
50	Arsenic	IRSL	0.0002	Annual	11.95	Wood boiler
50	Benzene	IRSL	0.1	Annual	4.56	Wood boiler
50	Chromium VI	IRSL	8.5E-5	Annual	4.58	Wood boiler
50	Formaldehyde	IRSL	0.08	Annual	5.97	Wood boiler
50	Manganese	ITSL	0.05	annual	3.48	Wood boiler
50	Silver	ITSL	0.1	8 hr	16.62	Wood boiler
100	Acrolein	ITSL	0.02	annual	28.78	Wood boiler
100	Acrolein	ITSL	5	1 hr	1.15	Wood boiler
100	Arsenic	IRSL	0.0002	Annual	15.83	Wood boiler
100	Benzene	IRSL	0.1	Annual	6.04	Wood boiler
100	Chromium VI	IRSL	8.5E-5	Annual	6.07	Wood boiler
100	Formaldehyde	IRSL	0.08	Annual	7.91	Wood boiler
100	Manganese	ITSL	0.05	annual	4.60	Wood boiler
100	Nickel	IRSL	0.0042	Annual	1.13	Wood boiler
100	Silver	ITSL	0.1	8 hr	22.02	Wood boiler
500	Acrolein	ITSL	0.02	annual	101.80	Wood boiler
500	Acrolein	ITSL	5	1 hr	4.07	Wood boiler
500	Arsenic	IRSL	0.0002	Annual	55.99	Wood boiler
500	Benzene	IRSL	0.1	Annual	21.38	Wood boiler
500	Benzo (a) pyrene	IRSL	0.0005	Annual	2.65	Wood boiler
500	Beryllium	IRSL	0.0004	Annual	1.40	Wood boiler
500	Cadmium	IRSL	0.0006	Annual	3.48	Wood boiler
500	Chlorine	ITSL	0.3	annual	1.34	Wood boiler
500	Chromium VI	IRSL	8.3E-5	Annual	21.46	Wood boiler
500	Chromium VI	ITSL	0.008	24 hr	1.34	Wood boiler
500	Formaldehyde	IRSL	0.08	Annual	28.00	Wood boiler
500	Formaldehyde	ITSL	9	8 hr	2.24	Wood boiler
500	Manganese	ITSL	0.05	annual	16.29	Wood boiler
500	Nickel	IRSL	0.0042	Annual	4.00	Wood boiler
500	Silver	ITSL	0.1	8 hr	77.86	Wood boiler
500	Total Dioxin TEQ****	IRSL	2.3E-08	Annual	2.66	Wood boiler

<sup>\*</sup>Screening Level: Initial Threshold Screening Level (ITSL); Initial Risk Screening Level (IRSL)

<sup>\*\*</sup> AT = Averaging Time associated with Screening Level

<sup>\*\*\*</sup>cancer risk in 1 million, or noncancer Hazard Quotient

<sup>\*\*\*\*</sup> The EF for total dioxin TEQ is based on a boiler with a multicyclone air pollution control device. It was assumed that very little dioxin-like compounds would be captured using this device, therefore, it was deemed appropriate to use this EF as an "uncontrolled" process for the purposes of this assessment. EPA (WebFire) has EF for uncontrolled wood boilers for dioxins congeners which group dioxins by chlorine number. AQD was unable to allocate carcinogenic potency of these groupings because not all the individual congeners within a group are carcinogenic and/or do not have relative potency factors.

#### D. Biodiesel Fired Boilers

EPA does not have EFs for biodiesel in WebFIRE. A study by EPA (2008) was performed and the resulting EFs were used for this exercise. A total of 157 TAC Emission Factors were available for biodiesel fired boilers burning either soy or animal biodiesel. EFs for metals and acrolein were not available for biodiesel boilers. Another study (Cosseron et al., 2011) seems to indicate that carbonyl compounds may be emitted at a higher rate than for petroleum diesel. The TACs that had maximum modeled impacts exceeding an ITSL or IRSL were as follows:

Source Size (MMBTU/hr)	Chemical Name	SL* Type	SL (µg/m³)	AT**	Magnitude of SL exceedance***	Biodiesel Boiler Fuel Type
50	Formaldehyde	IRSL	0.08	Annual	4.19	SOY
100	Formaldehyde	IRSL	0.08	Annual	5.55	SOY
500	Formaldehyde	ITSL	9	8 hr	1.57	SOY
500	Formaldehyde	IRSL	0.08	Annual	19.62	SOY
500	Acetaldehyde	ITSL	9	24 hr	1.15	SOY
500	Acetaldehyde	IRSL	0.5	Annual	3.45	SOY
500	Formaldehyde	IRSL	0.08	Annual	1.88	Animal

#### DISCUSSION

The possibility of exempting certain sources that burn clean fuel from the toxics rules was evaluated by attempting to quantify ambient air concentrations of toxic air contaminants at a hypothetical fence-line and the potential for adverse human health impacts. Certain assumptions were made as to the location of the smoke stack and the distance to the fenceline. Air dispersion modeling was performed using AERSCREEN. It was also assumed that larger sources would have taller stacks. Long-term cancer health impacts and both acute and chronic non-cancer health impacts were estimated by comparing the air concentration at the fenceline to AQD screening levels. Screening levels have uncertainty because they are based on and the available relevant toxicology datasets that are rarely complete, necessitating the use of uncertainty factors to help ensure protection over a lifetime for all groups, including sensitive subgroups. Exposure assumptions may also be conservative. Chronic screening levels for TACs that cause non-cancer effects have 24 hour or annual average times, and exposure can be for a life-time (typically 70 year duration). Short-term (acute) SLs are designed to be protective for exposure occurring over a 24-hr period or less and can also have averaging times of 8-hr and 1-hr depending on the critical health endpoint found to be the most sensitive. TACs that can cause cancer are treated as if any concentration can increase the possibility of contracting cancer.

The severity of harm to human health from TAC exposures at the fenceline is not easily assessed because of the limitations in the data used to derive the SL, and other uncertainties related to exposure. Exposure uncertainties come from the emission factors used to estimate the emissions, the air dispersion model, and the likelihood of humans, including sensitive individuals, to be at the fenceline for the time period (averaging time) associated with the TAC SL.

Only the TACs that exceeded health benchmarks are shown in the Tables above. Because it has not been previously explained in this report, recall that TACs that are assumed to cause cancer have IRSLs. TACs can have more than one non-cancer SL because different

durations of exposure can cause different health effects, each having its own threshold. Each TAC impact and significance of exceeding the SL is discussed below.

#### **NONCARCINOGENS**

Eight TACs had ITSLs that were exceeded when impacts were calculated for size, fuel and process types.

## 1) Acrolein

- a. Acrolein Acute SL: 5 µg/m³ with a 1-hr averaging time
  - i. The Acute SL for acrolein was exceeded for these fuels and size processes:

Fuel Size		PAI* (µg/m³)	Ratio of PAI/ITSL	Ratio of PAI/14 µg/m³	
Wood	Medium	5.76	1.2	0.41	
Wood	Large	20.36	4.1	0.60	
Nat Gas	Small	8.45	1.7	0.80	
Nat Gas	Medium	11.20	2.2	1.45	
Nat Gas	Large	39.60	7.9	2.83	

- ii. The basis of the acute acrolein ITSL is a study where 36 healthy human (student) volunteers were exposed (eyes only) to 140 µg/m³ for 5 minutes. Severity of eye irritation was measured subjectively in test subjects and controls as 0=no irritation, 1=mild and 2=severe. The low dose of 140 µg/m<sup>3</sup> had an average irritation score of 0.47 compared to control subjects of 0.36. No statistical analysis was performed. The ITSL derivation included an uncertainty factor of 3 to account for mild irritation effects at the low dose. After reviewing the basis of the acute ITSL, an assessment of the significance of the impacts exceeding the ITSL could consider the minimal effects that potentially occurred at this level, and the average irritation score of 1.2 reported at the next higher exposure level of 3380 µg/m<sup>3</sup>. An alternative benchmark could be calculated as 140 µg/m³ divided by a 10-fold uncertainty factor for protection of sensitive individuals and duration uncertainty. The more evident irritancy at 3380 µg/m³ was based on an average eye irritation score of 1.2, which is slightly higher than mild irritation. The Large Natural Gas Reciprocating Engine scenario with impact of 39 µg/m³ would be approximately 86 times lower than this level (3380/39).
- b. Acrolein Chronic SL: 0.02 μg/m³ with an annual averaging time.
  - i. Fuel, Size and Process Scenarios

Fuel	Size	Worst Process	PAI (µg/m3)	Ratio PAI to ITSL
Diesel	Large	Reciprocating Engine	0.05	2.4
Wood	Small	boiler	0.43	21.7
Wood	Medium	boiler	0.58	28.8
Nat Gas	Small	Reciprocating Engine	0.84	42.2
Nat Gas	Medium	Reciprocating Engine	1.12	56.0
Wood	Large	boiler	2.04	101.8
Nat Gas	Large	Reciprocating Engine	3.96	198.0

ii. The chronic ITSL for acrolein is based on an EPA RfC, which is based on a subchronic (3 month) rat inhalation study. Histopathologic changes described as "slightly affected" were found in the nasal cavity of 1 of 12

rats exposed to the lowest dose of 0.4 ppm (0.9 mg/m3). The duration adjusted LOAEL (6 hours per day; 5 days per week; 6/24x5/7) = 160 µg/m<sup>3</sup>. A total uncertainty factor of 1000 was applied. The animal dose was also adjusted to a human equivalent concentration using a regional gas dose ratio (RGDR) of 0.14. However, recent EPA guidance states that acrolein is among one of a number of compounds that act on the nasal passages via a mechanism in which the RGDR should be equal to 1 (i.e., the dose in rats equals the dose in humans). A more up-to-date ITSL reflecting this change in the EPA recommended risk assessment approach would therefore be 0.16 µg/m³ with an annual averaging time. The AQD will proceed to make that change to the ITSL. An additional observation could be made about the NOAEL/LOAEL designation of the 900 µg/m<sup>3</sup> dose as a LOAEL. Only 1 of 12 rats had slight irritation at 900 ug/m³, which could be interpreted to be indicative of a NOAEL. If the 900 µg/m³ exposure was regarded as a NOAEL then an alternative ITSL calculation could include uncertainty factors of  $UF_A = 3$  (animal to human) and  $UF_H = 10$  (for sensitive individuals), and  $UF_S = 10$  (subchronic to chronic). The resulting total UF = 300, and the resulting benchmark = 3 μg/m³. The highest impact scenario comes from the large natural gas reciprocating engine scenario, with a fenceline ambient air concentration of ~4 µg/m³ (annual averaging time). This analysis of the underlying key study, application of uncertainty factors, and potential alternative ways of interpreting the data suggest that the maximum modeled impacts pose a fairly low potential risk of nasal irritant effects.

- 2) Butadiene: Chronic ITSL =  $2 \mu g/m^3$  with 24-hr averaging time.
  - a. The ITSL was modestly exceeded for one scenario: Large Natural Gas Reciprocating engine at 2.5 μg/m³.
  - b. According to Rule 232(21)(a), the 24-hr averaging time is applied to the EPA RfC of 2 μg/m³ which is the basis of the ITSL. Because EPA used a long-term study as the basis of the RfC and applied methodology consistent with calculating a long-term health benchmark (i.e., chronic) it is more appropriate to use an annual averaging time with the ITSL. If impacts are compared to 2 μg/m³ annual averaging time. The annual impacts for Butadiene are 0.4 μg/m³ and are below the SL.
- 3) Acetaldehyde: Chronic ITSL =  $9 \mu g/m^3$  with 24 hour averaging time.
  - a. The ITSL was modestly exceeded for one scenario: Large Natural Gas Reciprocating engine at 25.5 μg/m³. (2.83x above the ITSL)
  - b. According to Rule 232(21)(a), the 24-hr averaging time is applied to the EPA RfC of 9  $\mu$ g/m³ which is the basis of the ITSL. Because EPA used a long-term study as the basis of the RfC and applied methodology consistent with calculating a long-term health benchmark (i.e., chronic) it is more appropriate to use an annual averaging time with the ITSL. If impacts are compared to 9  $\mu$ g/m³ annual averaging time. The annual impacts for acetaldehyde are 4.3  $\mu$ g/m³ and are below the SL.
- 4) Chlorine: Chronic ITSL =  $0.3 \mu g/m^3$  with annual averaging time
  - a. The impact of  $0.4 \,\mu\text{g/m}^3$  modestly exceeded the ITSL for one scenario: Large wood fired boiler. This is  $1.3x \, \text{ITSL}$ .
  - b. The study used to derive the ITSL exposed rats to various concentrations of chlorine, the lowest dose of 0.4 ppm (1.1 mg/m³) produced significant nasal lesions. The benchmark dose methodology was used to extrapolate to a NOAEL of 0.2 mg/m³ (200 μg/m³), then duration adjusted (6/24x 5/7) to get 0.042 mg/m³

(42 μg/m³). A further adjustment was made to account for the differences between rat and human nasal dosimetry, with a factor of 0.2 for the regional gas dose ratio (RGDR) to obtain a point of departure of 8.4 μg/m³. A total UF of 30 was used: 3 for animal to human and 10 for sensitive individuals to get ITSL of 0.3 (rounded from 0.28 μg/m³). Recent analysis comparing the nasal region of rat to humans indicates, "a larger portion of inspired air passed through olfactory-lined regions in the rat than in the monkey or human." (Kimbell, 2006). Given that the rat nasal region gets a higher dose than humans then the RGDR should default to 1. If the RGDR of 1 is used, the RfC and ITSL would 1.4 μg/m³. The chlorine impact from large wood fired boilers is 0.4 μg/m³ and is less than the adjusted chlorine ITSL of 1.4 μg/m³

- 5) Chromium IV (hexavalent chromium): Chronic ITSL = 0.01 ug/m3 with a 24-hr averaging time.
  - a. Large wood fired boiler produced an impact of 0.0107  $\mu g/m^3$  with a 24-hr average.
  - b. As mentioned before the averaging time for chronic benchmarks is more appropriately coupled with an annual averaging time. The annual impact of Chromium IV is 0.00178 μg/m³, which is <the adjusted ITSL of 0.01 μg/m³ annual.
- 6) Formaldehyde: Acute ITSL = 9 ug/m³ with 8-hr averaging time
  - Large wood fired boiler produced an impact of 20 μg/m³ with a 8-hr average, which is 2.3x higher than ITSL.
  - b. The ITSL was derived from a human occupation study where workers were exposed 8-hrs/day for average of 10 years. The observed effects were: Nasal obstruction and discomfort, lower airway discomfort, and eye irritation at the LOAEL of 0.26 mg/m³. A NOAEL of 0.09 mg/m³ was also identified. The formaldehyde impact is roughly 3x lower than the NOAEL and 13x lower than the LOAEL.
- 7) Manganese: Chronic ITSL =  $0.05 \mu g/m^3$  annual averaging time
  - a. Fuel, process and size scenarios where impacts exceeded ITSL:

Fuel	Size	Worst Process	PAI Impacts (µg/m3)	Ratio to SL
diesel	Small	Engine Turbine	0.09	1.72
diesel	Medium	Engine Turbine	0.11	2.27
diesel	Large	Engine Turbine	0.40	8.04
wood	Small	boiler	0.17	3.48
wood	Medium	boiler	0.23	4.60
wood	Large	boiler	0.81	16.29

- b. The ITSL is based on an occupational study where neurological effects were observed at an effect level of 150  $\mu g/m^3$  was duration adjusted to 50  $\mu g/m^3$  and an uncertainty factor of 1000 was applied.
- 8) Silver: Acute ITSL =  $0.1 \mu g/m^3 8 hr$ 
  - a. Wood boilers of size Small, Medium and Large had impacts of 1.7, 2.2 and 7.8  $\mu g/m^3$ , respectively (ratio to ITSL = 17, 22 and 78, respectively).
  - b. The ITSL is based on an occupational exposure limit (OEL) of  $10 \,\mu g/m^3$  for soluble silver compounds in order to prevent argyria. Silver dust has an OEL of  $100 \,\mu g/m^3$ . The ITSL is derived by dividing the OEL by 100. Argyria is caused by chronic intake of silver resulting in an accumulation of silver or silver sulfide particles in the skin and eyes. Argyria is generally believed to be irreversible. It is a described as a "cosmetic problem" and is not physically harmful. The

American Conference of Governmental and Industrial Hygienists (ACGIH) stated that the photographic industry's use of silver nitrate indicated that no cases of argyria or other adverse effects have appeared where average exposures were about 40 to 60  $\mu g/m^3$  with values as high as about 150  $\mu g/m^3$ . The highest impact of 0.81  $\mu g/m^3$  below the OEL of 10  $\mu g/m^3$  and is below what is considered a no effect level of approximately 40  $\mu g/m^3$ .

## **CARCINOGENS**

Twelve TACs were modeled to have impacts that resulted in greater than 1 per million

incremental cancer risk for fuel, process type and size.

Fuel	€:=o	Chamiaal	IRSL	Waret Presses	PAI*	Risk per	Cammant
Fuel	Size	<b>Chemical</b> 1,1,2,2-	(µg/m³)	Worst Process	(µg/m3)	Million	Comment
Nat Gas	Large	Tetrachloroethane	0.02	Reciprocating Engine	0.034	2	<srsl< td=""></srsl<>
Nat Gas	Small	1,3-Butadiene	0.02	Reciprocating Engine	0.089	3	<srsl< td=""></srsl<>
Nat Gas	Medium	1,3-Butadiene	0.03	Reciprocating Engine	0.12	4	<srsl< td=""></srsl<>
Nat Gas	Large	1,3-Butadiene	0.03	Reciprocating Engine	0.42	14	COROL
Diesel	Large	Acetaldehyde	0.5	Reciprocating Engine	0.54	1.1	<srsl< td=""></srsl<>
Nat Gas	Small	Acetaldehyde	0.5	Reciprocating Engine	0.91	2	<srsl< td=""></srsl<>
Nat Gas	Medium	Acetaldehyde	0.5	Reciprocating Engine	1.2	2	<srsl< td=""></srsl<>
Soy BD	Large	Acetaldehyde	0.5	Boiler	1.7	3	<srsl< td=""></srsl<>
Nat Gas	Large	Acetaldehyde	0.5	Reciprocating Engine	4.3	9	<srsl< td=""></srsl<>
Diesel	Small	Arsenic	2E-4	Engine Turbine	0.0012	6	<srsl< td=""></srsl<>
Diesel	Medium	Arsenic	2E-4	Engine Turbine	0.0012	8	<srsl< td=""></srsl<>
Wood	Small		2E-4	Boiler	0.0016	12	CONOL
Wood	Medium	Arsenic	2E-4	Boiler		16	
		Arsenic	2E-4		0.0032		
Diesel	Large	Arsenic	2E-4 2E-4	Engine Turbine	0.0056	28	
Wood	Large	Arsenic		Boiler	0.011	56	0001
Diesel	Small	Benzene	0.1	Reciprocating Engine	0.10	1.01	<srsl< td=""></srsl<>
Diesel	Medium	Benzene	0.1	Reciprocating Engine	0.13	1.3	<srsl< td=""></srsl<>
Wood	Small	Benzene	0.1	Boiler	0.46	5	<srsl< td=""></srsl<>
Diesel	Large	Benzene	0.1	Reciprocating Engine	0.47	5	<srsl< td=""></srsl<>
Wood	Medium	Benzene	0.1	Boiler	0.60	6	<srsl< td=""></srsl<>
Wood	Large	Benzene	0.1	Boiler	2.1	21	
Wood	Large	Benzo (a) pyrene	5E-4	Boiler	0.0013	3	<srsl< td=""></srsl<>
Diesel	Medium	Beryllium	4E-4	Boiler	0.00043	1.1	<srsl< td=""></srsl<>
Wood	Large	Beryllium	4E-4	Boiler	0.00056	1.4	<srsl< td=""></srsl<>
Diesel	Large	Beryllium	4E-4	Boiler	0.0015	4	<srsl< td=""></srsl<>
Diesel	Medium	Cadmium	6E-4	Engine Turbine	0.00069	1.2	<srsl< td=""></srsl<>
Wood	Large	Cadmium	6E-4	Boiler	0.0021	3	<srsl< td=""></srsl<>
Diesel	Large	Cadmium	6E-4	Engine Turbine	0.0024	4	<srsl< td=""></srsl<>
Diesel	Small	Chromium (VI)	8.3E-5	Engine Turbine	0.00012	1.4	<srsl< td=""></srsl<>
Diesel	Medium	Chromium (VI)	8.3E-5	Engine Turbine	0.00016	2	<srsl< td=""></srsl<>
Wood	Small	Chromium (VI)	8.3E-5	Boiler	0.00038	5	<srsl< td=""></srsl<>
Wood	Medium	Chromium (VI)	8.3E-5	Boiler	0.00050	6	<srsl< td=""></srsl<>
Diesel	Large	Chromium (VI)	8.3E-5	Engine Turbine	0.00056	7	<srsl< td=""></srsl<>
Wood	Large	Chromium (VI)	8.3E-5	Boiler	0.0018	21	
Nat Gas	Small	Ethylene Dibromide	0.002	Reciprocating Engine	0.0080	4	<srsl< td=""></srsl<>
Nat Gas	Medium	Ethylene Dibromide	0.002	Reciprocating Engine	0.011	5	<srsl< td=""></srsl<>
Nat Gas	Large	Ethylene Dibromide	0.002	Reciprocating Engine	0.037	19	
Animal BD	Large	Formaldehyde	0.08	Boiler	0.15	2	<srsl< td=""></srsl<>
Diesel	Large	Formaldehyde	0.08	Reciprocating Engine	0.24	3	<srsl< td=""></srsl<>
Soy BD	Small	Formaldehyde	0.08	Boiler	0.33	4	<srsl< td=""></srsl<>
Soy BD	Medium	Formaldehyde	0.08	Boiler	0.44	6	<srsl< td=""></srsl<>
Wood	Small	Formaldehyde	0.08	Boiler	0.48	6	<srsl< td=""></srsl<>
Wood	Medium	Formaldehyde	0.08	Boiler	0.63	8	<srsl< td=""></srsl<>
Soy BD	Large	Formaldehyde	0.08	Boiler	1.6	20	JOINOL
Wood	Large	Formaldehyde	0.08	Boiler	2.2	28	
Wood	Medium	Nickel	0.0042	Boiler	0.0047	1.1	<srsl< td=""></srsl<>
vvoou	IVICUIUIII	TAIONOI	0.0042	סווכו	0.0047	1.1	<srsl< td=""></srsl<>

<sup>\*</sup> PAI = predicted ambient impact is the maximum modeled air concentration

Most of the impacts resulted cancer risk that was less than 1 per 100,000 risk level, and all the TACs had impacts less than 1 per 10,000 risk level.

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